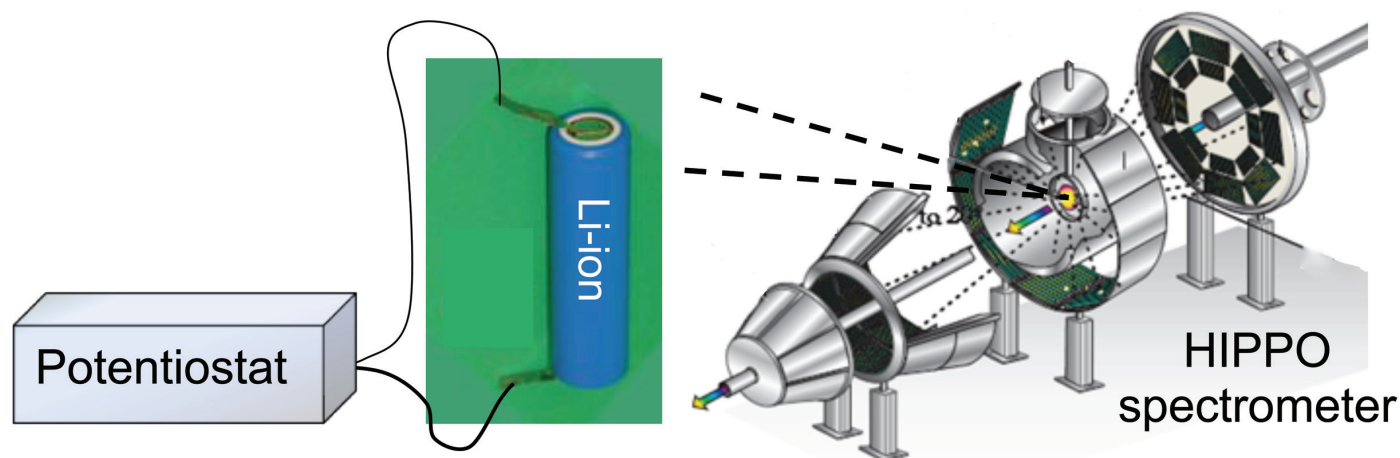# Materials Science and Technology
Materials Characterization

In-Situ Neutron Diffraction of Li-Ion Batteries

Figure 1: A standard cylindrical 18650-type Li-ion battery (LPF-1350, 2.5 Ah) was electroded to a potentiostat and cycled *in-situ* within the HIPPO neutron spectrometer at LANSCE in Los Alamos National Laboratory.

Time dependent materials analysis of charge/ discharge cycles will lead to improved electrical energy storage

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In an era where electrical energy storage is becoming increasingly important, the understanding of electrochemical reactions in batteries is crucial. A science-based approach to understanding these reactions can lead to breakthroughs in battery capacity and performance. As a means of energy storage, batteries will need significant improvement in order to support the continually increasing demands of electric vehicles as well as portable electronics.

Sandia has been developing protocols that allow for diagnosis of electrochemical cell reactions "*in-situ*," that is, methods for monitoring a battery while it is undergoing charging and discharging. Typical materials science diagnostic techniques are not usually designed to accommodate this approach. Instead, a charge-discharge experiment would be performed on many batteries, each run to a given state-of-charge (SOC), followed by disassembly. The disassembled battery parts would be investigated in what is often termed a "post-

mortem" analysis. However, such analyses do not always reflect the dynamic behavior of a battery system. Dynamic behavior is best obtained by the *in-situ* method.

In-situ measurements can be quite challenging. First of all, one must be able to collect data rapidly in order to capture changes while they are occurring. Another complication often arises from overlapping data. A dataset (e.g., a diffraction pattern) usually contains information from many different parts of a battery (anode, cathode, separator, electrolyte, external casing, etc). One must be able to sift through the results to isolate the signal associated with battery performance from signal that is irrelevant (and therefore unwanted). This is often so difficult that such attempts are abandoned in favor of post-mortem work. Early on, Sandia employed in-situ X-ray diffraction (XRD) analysis and has been able to overcome signal extraction issues by the use of multivariate analysis (MVA) techniques[1]. However, the XRD experiments required a specially-designed "coffee-bag" battery, since
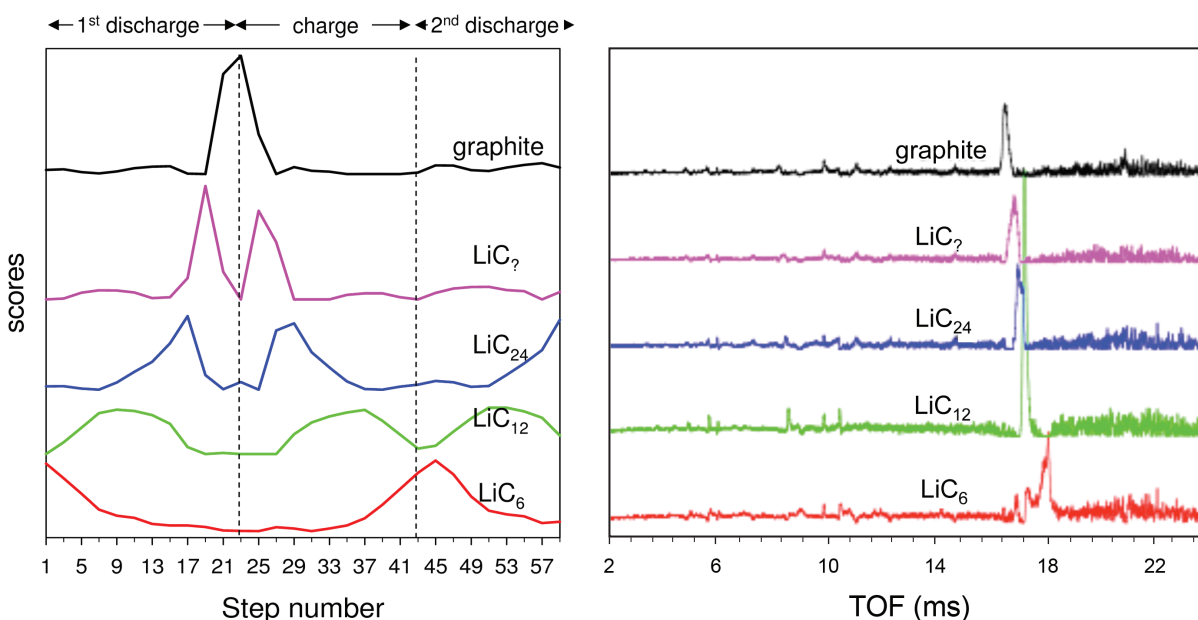
Figure 2: (*Left*) MVA scores with step number of neutron scattering analysis during Li-ion battery discharging and charging cycles. (*Right*) MVA-derived neutron diffraction histogram components from corresponding MVA analysis.

the X-ray beam cannot penetrate the outside containers of typical commercial batteries[1].

The problem of the outer packaging was solved by the use of highly penetrating neutron beams. Recent development of a neutron time-of-flight powder diffractometer called HIPPO (for High-Pressure-Preferred Orientation) at the Los Alamos Neutron Science Center (LANSCE) provides both a neutron scattering capability, along with sufficiently fast data collection for monitoring of the electrochemical behavior of a commercial battery. Sandia researchers and their Los Alamos collaborators chose a standard 18650 cylindrical Li-ion battery for their experiment (see Figure 1). A fully-charged battery was placed in the spectrometer and neutron diffraction data were collected during electrochemical cycling. By employing the use of MVA, the researchers were able to screen out noise and unwanted signal to reveal information about the ongoing chemical changes occurring in the cell. The cell was discharged, recharged, and discharged again.

Figure 2 shows the results for the anode behavior, with isolated component histograms from time-of-flight neutron diffraction (right side of figure) along with their corresponding scores (left). The histograms show strong peaks that are characteristic of lithium carbide (LiC_x) compounds (where x = 6, 12, etc). The neutron scattering scores are output from MVA, and can be thought of as proportional to concentration. The x-axis for the scores plot represents the step number and refers to the SOC of the battery at the time of measurement. These steps were roughly 10% of the battery's capacity. As one can see from Figure 2 (e.g., steps 1-23 in the first discharge), the various phases occur stepwise starting with LiC_6 at full charge

followed by LiC_{12}, LiC_{24} and concluding with graphite devoid of Li upon complete discharge. This stepwise process, or "staging," is known to occur in graphitic Li-ion anodes[2]. What has not been documented is an additional phase (labeled $LiC_?$) that may be a possible LiC_{48} compound according to the component data (Figure 2 right); the new phase appears to be stable just before complete discharge. This new phase, precipitated from the multivariate analysis, has typically eluded detection. Likewise, additional analysis (not shown) successfully measured the simultaneous and complimentary reaction of $FePO_4$ to $LiFePO_4$ in the cathode of the battery.

The combination of *in-situ* analysis with the powerful MVA techniques shows promise for the dynamical diagnosis of functioning electrochemical cells, and should greatly enhance the understanding of batteries as entire systems. Future work will explore failure mechanisms of batteries and obtain heretofore overlooked subtleties regarding battery function that may be crucial in battery advancement.

References:

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2. Billaud, D., McRae, E. & Herold, A. (**1979**). "Synthesis and Electrical Resistivity of Lithium-Pyrographite Intercalation Compounds (Stages I, II, and III)," *Mat. Res. Bull.*, **14**, 857-864.